
(12) UK Patent Application (19) GB (11) 2 380 231 (13) A

(43) Date of A Publication 02.04.2003

(21) Application No 0123060.6	(51) INT CL ⁷ B65D 83/14
(22) Date of Filing 26.09.2001	(52) UK CL (Edition V) F1R RBB RCX RDX
(71) Applicant(s) Reckitt Benckiser N.V. (Incorporated in the Netherlands) Kantoorgebouw de Appelaar, De Fruittinen 2-12, 2132 NZ Hoofddorp, Netherlands	(56) Documents Cited GB 0719647 A WO 2001/027351 A WO 1997/010802 A JP 110302637 A US 5032318 A ROCKAFORT, Spray Technology & Marketing Dec 1995, PreventingCorrosion in Aqueous Based Aerosols
(72) Inventor(s) Mattia De Dominicis Zefferino Righetto	(58) Field of Search UK CL (Edition S) F1R RBB RCX RDX INT CL ⁷ B65D 83/14, C23F 11/12 Other: ONLINE: WPI; EPODOC; JAPIO; FULL-TEXT
(74) Agent and/or Address for Service Andrew Stephen Brown Reckitt Benckiser plc, Group Patents Departments, Dansom Lane, HULL, HU8 7DS, United Kingdom	

(54) Abstract Title
Corrosion inhibitors for tin plated aerosol canisters

(57) An aerosol product comprising a tin plated, optionally lacquered cannister, a propellant, an active formulation and a cannister corrosion inhibitor wherein the cannister corrosion inhibitor comprises a silicate.

GB 2 380 231 A

CORROSION INHIBITORS FOR LACQUERED AND
UNLACQUERED TIN PLATED AEROSOL CANISTERS

5

BACKGROUND OF THE INVENTION:

Many products designed for household, hard surfaces, fabric care, carpet cleaners are sold in aerosol containers. A few aerosol products are sold in glass or plastic containers. Most containers are metal canisters, most canisters are steel, usually tin coated, others are aluminium. Tin coated metal canisters may also be lacquered with a resin on the inside to provide additional protection.

Examples of aerosol products are air fresheners, car products, household products, fabric care, waxes, polishes, insecticides, ironing aides, fabric refreshers, and carpet cleaners.

Tin coating protects the metal canisters against rapid corrosion, but tends itself to dissolve in water based formulations, depending on the composition and storage conditions. With aerosol formulae containing less than 50 ppm of water, corrosion of tin plated canisters is not generally a serious problem. However, if the water content of an aerosol product is more than 50 ppm, problems due to corrosion are more likely to occur.

The world market trend is to move towards water based aerosol formulations. This is due mainly to a regulatory issue; the reductions of the volatile organic content (VOC) levels in aerosol product has involved the 5 reduction of the solvent level in many products and an increase of the water content.

Many corrosion inhibitor systems have been developed for the new market requirements in aerosol products, 10 especially for tin plated canisters. Examples of these products are borates, benzoates, molybdate, and surfactants (such as sodium louroyl sarcosinate. The best recognised inhibitor system for tin plated canisters is formed, in any case, by sodium nitrite and morpholine. 15 Morpholine is a volatile base that helps to preserve the vapour phase in the aerosol containers and gives an alkaline pH to the formula. This system can involve the formation of nitrosamines that are very carcinogenic. In addition, even sodium nitrite and morpholine are not 20 generally able to prevent the dissolution of the tin coating, but to reduce the rate of dissolution of the tin coating to an acceptable level. The amount of morpholine, sodium nitrate and thickness of tin plate are designed for around the required shelf life, for example 25 two years. The dissolution of the tin plate to form a tin hydroxyl-oxide complex has been shown to have a negative effect on cleaning performances. The tin complex generally gives a pale yellow to an intense yellow colour when deposited, especially when sprayed 30 onto a white surface. White fabrics or carpets can remain coloured by the liquids of aged aerosol products. Other considerations relate to certain stains like

coffee, tea and wine that contain cationic metals. These metals can form brown coloured complex with tin hydroxyl-oxide complex, causing an evident negative effect of the cleaning formulation and its overall cleaning
5 performance.

Even resin lacquered tin-plated canisters generally need an effective corrosion system. Possible defects on the lacquer layer are the cause of pit corrosion: the
10 galvanic potential is discharged in a limited area, involving a quick and deep corrosion. Even sodium nitrite and morpholine, cannot prevent dissolution of the lacquer and tin plate, the liquid becomes yellowish and the interior can darken. This system is in addition to
15 be avoided for nitrosamine formation during the product life.

SUMMARY OF THE INVENTION:

20 Many corrosion inhibitors have been identified in prior art, but are not able to stop the dissolution of the tin layer in a tin plated aerosol canister over the two year standard can life.

25 It has been surprisingly found that silicates are very effective corrosion inhibitors for tin plated or lacquered tin plated aerosol canisters. If they are combined with a base which is volatile at room temperature they form a complete corrosion inhibitor
30 systems, which is also able to preserve the canister in the vapour phase. What has been found is that silicates preserve the tin layer, leaving it with a mirror

appearance even after six months of storage stability at 40°C. This unexpected discovery avoids almost all the negative defects of the existing corrosion inhibitors:

- 5 • No toxicological impact. Silicates are effective as corrosion inhibitors at the very low concentration and they don't have any impact on the final formulation toxicological profile, neither are they involved in nitrosamine formation.
- 10 • They avoid the yellowing of the formulation caused by the dissolution of the tin layers and the connected negatives related to stain removal.
- 15 • The interior canister appearance remains completely preserved.
- 20 • Limits the pit corrosion in case of non homogeneously applied lacquered resin protective layer.
- 25 • Avoids the formation of solid particles deriving from tin dissolution. The tin dissolution can generate tin hydroxyl/oxide non soluble complexes. These complexes tend to form solid particles that can block the valve/actuator during spraying or in any case they can affect the proper spraying product characteristics.

Other advantages of silicates are that they are very effective even at low concentration, starting from 0.01% wt.

5 Other relevant characteristic is their low cost and low impact on the overall formula cost.

By the use of the term "room temperature" we mean at $<30^{\circ}\text{C}$, $<25^{\circ}\text{C}$, $<20^{\circ}\text{C}$ or $<15^{\circ}\text{C}$.

10 Suitable volatile bases are selected from primary, secondary, tertiary and quartenary amines; preferred amines are primary and quartenary amines, especially ammonia.

15 **DETAILED DESCRIPTION:**

20 Broadly a large number of silicates can be used "characterised by the presence of the elements silicon, oxygen, and one or more metals with or without hydrogen" - quoted from The Condensed Chemical Dictionary, 6th Edition, Reinhold Publishers.

25 A preferred silicate is defined by either of the following formula:

30 $x\text{SiO}_2:y\text{M}_2\text{O}$, where M is Na, K or Li and x:y is the molar ratio between SiO_2 and M_2O and is a ratio of from 0.1:1 to 10:1, preferably from 1.6:1 to 4:1; or

$x\text{SiO}_2:y\text{M}_2\text{O}:z\text{Al}_2\text{O}_3$, where M is defined above and x:y:z is the molar ratio between SiO_2 , M_2O and Al_2O_3 , and each x, y or z is independently a number in the range 0.1 to 10.

5 The performance of the new corrosion inhibitor system has been compared with a lot of known systems available on the market. To evaluate the performances a real condition canister storage test has been carried out. A quick method that avoids the need to gas the
10 canister has been identified for preliminary corrosion behaviour evaluation, the jar method.

JAR METHOD

15 50ML glass jars with screw plugs are used in this test.

20 A round piece of canister is cut and applied on the internal surface of the jar screw plug. A poly tetra fluoroethylene gasket is also applied on the plug in order to guarantee a good sealing system. The jar is filled with the testing formula and it is stored in the inverted position for obtaining the contact between the liquid formula and the tin plated canister piece applied
25 on the plug. The stress test is carried out in an oven at 50°C for several days up to 1 month and a cross is cut by a blade on the canister piece in order to simulate possible defects on the canister walls.

30

The storage situation is monitored after 1 day, 1 week, 2 weeks, and 1 month and compared to reference

canister pieces and liquids. The canister piece and liquid appearances are recorded. A recording data table with the corresponding corrosion rating is reported below:

5

Corrosion Rating JM	Canister piece appearance	Liquid appearance
0	No difference from reference	No difference from reference
1	Low darkening along the cut lines	No difference from reference
2	Darkening along the cut lines	No difference from reference
3	Low darkening on all the canister piece area	No difference from reference
4	Darkening on all the canister piece area	No difference from reference
5	Darkening on all the canister piece area	Pale yellowish of the liquid
6	Evident darkening on all the canister piece area	Yellowish of the liquid
7	Rust points	Rust

The higher the rating number then the worse the corrosion inhibitor system efficiency.

10

STORAGE TEST:

The storage test was carried out using final product conditions. Unlacquered and lacquered tin-plated 15 canisters were filled with the formula under evaluation and gassed with the propellant.

The samples under evaluation were stored at 5, 20 and 40°C for up to 6 months or at least at 40°C, considered as the condition at which the corrosion reactions are quicker. The canisters were placed in an upright or inverted position to evaluate the efficacy of the silicates versus the entire canister and valve components during the storage test.

At scheduled storage time, two canisters in the inverted and two in the upright position are de-gassed, opened and the liquid phase and interior can appearance evaluated. The storage test corrosion rating is described in the table below:

Corrosion Rating ST	Canister/valve appearance	Liquid appearance
A	No difference from reference	No difference from reference
B	Low darkening	No difference from reference
C	Darkening	No difference from reference
D	Darkening	Pale yellowish of the liquid
E	Evident darkening	Pale yellowish of the liquid
F	Evident darkening	Yellowish of the liquid
G	Evident darkening	Yellowish of the liquid with solid residue
H	Rust points	Rust
I	Rust points with canister leakage	Rust

15

EXAMPLES :

The liquid phases are typically prepared by mixing all the components together in a suitable container to form

a concentrate, placing an amount of the concentrate in a suitable container useful to dispense aerosols, and then the propellant is added. Examples of compositions forming a part of the present invention are set forth 5 below in Table 1, 2 and 3 with the various components identified in Table 4.

Components	Table 1					
	Ref 1	Ref 2	Ref 3	Ref 4	Ref 5	Ex 1
	%	%	%	%	%	%
Monawet SNO-35	2.860	2.860	2.860	2.860	2.860	2.860
Zonyl 7950	0.700	0.700	0.700	0.700	0.700	0.700
zelan 338	0.150	0.150	0.150	0.150	0.150	0.150
Hexyl cellosolve	0.750					
Dowanol PnP		0.750	0.750	0.750	0.750	0.750
Sodium citrate	0.114	0.114	0.114	0.114	0.114	
Citric acid						0.114
Preservative	0.100	0.100	0.100	0.100	0.100	0.100
Fragrance	0.134	0.134	0.134	0.134	0.134	0.134
Sodium nitrite	0.100					
Crystal 0075						0.200
Sodium benzoate			0.300	0.300		
Sodium molybdate					0.100	
Monacor BE				0.300		
Ammonium	0.007	0.007	0.007	0.007	0.007	0.007
DI water	95.085	95.085	94.88	94.585	95.085	94.915

The liquid formulation reported on table 1 were 10 gassed with butane propellant with a ratio concentrate/propellant = 93/7 wt/wt, double lacquered canisters were used.

Components	Table 2					
	Ref 6	Ref 7	Ref 8	Ref 9	Ex 2	Ex 3
	%	%	%	%	%	%
Texapon 101 AR	7.514	7.514	7.514	7.514	7.514	7.514
Crodasinic LS30	2.496	2.496	2.496	2.496	2.496	2.496

Incromine oxide S	2.898	2.989	2.989	2.989	2.989	2.989
Sodium nitrite	0.100					
Dowanol PnP						
Citric Acid					0.0087	
Crystal 0075					0.05	0.05
Sodium benzoate			0.075	0.075		0.0375
Monacor BE			0.075			0.0375
Morpholine	0.100	0.100				
Ammonium			0.0125	0.025	0.025	0.0062
DI water	86.801	86.901	86.8385	86.901	86.9173	86.8698

The liquid formulation reported on table 2 were gassed with butane propellant with a ratio concentrate-propellant=94/6 wt/wt, unlacquered canisters were used.

5

Components	Table 3				
	Ref 10	Ex 4	Ref 11	Ref 12	Ex 5
	%	%	%	%	%
Dowanol PnP			17.00	17.00	17.00
Dowanol DPnB	4.50	4.50			
Dowanol DPM	12.50	12.50			
Genapol 26-L-60			0.20	0.20	0.20
Genapol 26L-80	0.20	0.20			
Crystal 0075		0.20			0.20
Sodium benzoate	0.60	0.30	0.30	0.30	0.30
Monacor BE	0.80	0.50		0.80	0.50
Eltesol SC40	2.50	2.50			
Ammonium	0.05	0.05	0.05	0.05	0.05
DI water	78.85	79.25	82.45	81.65	81.75

The liquid formulation reported on Table 3 were gassed with butane propellant with a ratio concentrate/propellant = 94/6 wt/wt, unlacquered canisters were used.

Table 4	
Component	Description of component
Monawet SNO-35	Na4DicarboxyethylStearylSulfosuccinate from Uniqema
Zonyl 7950	Fluorosurfactant from Dupont
Zelan 338	Acrylic polymer from Dupont
Hexyl cellosolve	Ethylene Glycol Monohexyl Ether
Dowanol PnP	2-Propoxy propanol from Dow Chemical
Sodium citrate	Na citrate
Citrate acid	Citric acid
Preservative	Preservatives from various supplier
Fragrance	Fragrances from variou supplier
Sodium nitrite	Sodium nitrite
Crystal 0075	Silicate
Sodium benzoate	Sodium benzoate
Sodium molybdate	Sodium molybdate
Dowanol DPM	Depropylene glycol methyl ether from Dow Chemical
Genapol 26-L-60	Primary alcohol ethoxylate from Hoechst Celanese
Genapol 326-L-80	Primary alcohol ethoxylate from Hoechst Celanese
Eltesol SC40	Sodium cumene sulfonate 40% from Albright & Wilson
Texapon 101 AR	Sodium lauryl sulfate from Henkel
Crodasinic KS39	Sodium lauroyl sarcosinate from Croda
Incromine oxide S	Stearyl dimethylamine oxide
Morpholine	Morpholine
Ammonium hydrixide	Ammonium hydroxide
DI water	Deionized water

EXAMPLE RESULTS:

The silicate corrosion inhibitor system has been tested for all formulations previously described in terms of the Jar method and real condition storage stability.

Results for table 1 formulations:

Product	Corrosion rating (Jar method)			
	1 day	1 week	2 weeks	1 month
Ref 1	1	2	2	2-3
Ref 2	1	2	2	3
Ref 3	0	1	1	2
Ref 4	0	1	1	1-2
Ref 5	1	1	2	3
Ex 1	0	0	0	0

5

Product	Corrosion rating (Storage test)			
	1 month		2 months	
	T=20 °C	T=40 °C	T=20 °C	T=40 °C
Ref 1	A	C		
Ref 2	A	C		
Ref 3	A	C		
Ref 4	B	C		
Ref 5	A	D		
Ex 1	A	A		

10

Results for table 2 formulations

Product	Corrosion rating (Jar method)			
	1 day	1 week	2 weeks	1 month
Ref 6	4	6	6	6
Ref 2	3	6	6	6
Ref 7	3-4	5	6	6

Ref 8	3	4-5	6	6
Ref 9	3	4-5	6	6
Ex 2	0	0	0	0
Ex 3	0	0	0	0

5

Product	Corrosion rating (Storage test)			
	1 month		2 months	
	T=20 °C	T=40 °C	T=20 °C	T=40 °C
Ref 6	C	H	F	H
Ref 7	D	D	F	F
Ref 8	C-D	D	F	F
Ref 9	C-D	H	F	H
Ex 2	A-B	A-B	C	C
Ex 3	A-B	A-B	C	D

Results for table 3 formulations:

10

Product	Corrosion rating (Storage test)					
	6 weeks		3 months		6 months	
	T=20 °C	T=40 °C	T=20 °C	T=40 °C	T=20 °C	T=40 °C
Ref 10	C	D	D	G	E	H
Ex 4	A	A-B	A	A-B	A	A-B
Ref 11	C-D	D-E	D	D-E	E	F
Ref 12	D	D-E	D	D-E	E	E-F
Ex 5	A	A-B	A	A-B	A	A-B

15

CLAIMS

1. An aerosol product comprising:
 - 5 a) a tin plated, optionally lacquered canister;
 - b) a propellant;
 - c) an active formulation; and
 - d) a canister corrosion inhibitor characterised in
10 that the canister corrosion inhibitor comprises
a silicate.
2. An aerosol product as claimed in claim 1 wherein the
silicate contains the elements silicon, oxygen and
one or more metals with or without hydrogen.
15
3. An aerosol product as claimed in claim 3 wherein the
silicate is defined as
20 $x\text{SiO}_2:y\text{M}_2\text{O}$, where M is Na, K or Li and x:y is
the molar ratio between SiO_2 and M_2O and is a
ratio of from 0.1:1 to 10:1, preferably from
1.6:1 to 4:1; or
25 $x\text{SiO}_2:y\text{M}_2\text{O}:z\text{Al}_2\text{O}_3$, where M is defined above and
x:y:z is the molar ratio between SiO_2 , M_2O and
Al₂O₃, and each x, y or z is independently a
number in the range 0.1 to 10.
4. An aerosol product as claimed in any preceding claim
which has an active formulation and /or propellant
30 which has more than 50ppm & water.

- 5 An aerosol product as claimed in any preceding claim which additional comprises a base which is volatile at room temperature.
- 6 An aerosol product as claimed in claim 5 in which the base is a primary, secondary, tertiary or quartenary amine.
- 5
- 7 An aerosol product as claimed in claim 6 in which the base is ammonia. .
- 10
- 8 A method of preventing corrosion of a tin plated, and optionally lacquered, aerosol canister which method comprises adding a silicate to the propellant and/or active formulation within the canister.



Application No: GB 0123060.6
Claims searched: 1 - 8

16

Examiner: David Hotchkiss
Date of search: 31 October 2001

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.S): F1R (RBB, RCX, RDX)
Int Cl (Ed.7): B65D (83/14); C23F (11/12)
Other: Online: WPI; EPODOC; JAPIO; FULL-TEXT

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 719647 A (Colgate - Palmolive) Whole document especially page 4 lines 17 - 38	1
X	WO 01/27351 A1 (Unilever Plc) Whole document especially page 1 last paragraph.	1
X	WO 97/10802 A1 (Phylomed Corporation) Whole document especially page 18 step 5	1
A	US 5032318 (Philip L Bartlett) Whole document	
A	JP 11302637 (Earth Chem Corp Ltd) English abstract	
X	(Rocafort) Preventing Corrosion in Aqueous based Aerosols Spray Technology and Marketing - December 1995	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.